J. Serb. Chem. Soc. 69 (6) 455–460 (2004)
JSCS – 3172

UDC 678–13:539.217+546.9
Original scientific paper

Noble metals binding on macroporous poly(GMA-co-EGDMA) modified with ethylenediamine

ALEKSANDRA NASTASOVIĆ[1*#], SLOBODAN JOVANOVIĆ[2#], DRAGICA JAKOVLJEVIĆ[1#], SLAVKA STANKOVIĆ[2] and ANTONIJE ONJIA[3#]

[1]ICTM - Center for Chemistry, Njegoševa 12, Belgrade (e-mail: anastaso@helix.chem.bg.ac.yu), [2]Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade and [3]Vinča Institute of Nuclear Sciences, Chemical Dynamics Laboratory, P. O. Box 522, Belgrade, Serbia and Montenegro

(Received 28 July 2003, revised 8 January 2004)

Abstract: Macroporous crosslinked poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate), p(GME), was synthesized by suspension copolymerization and modified by reaction of the pendant epoxy groups with ethylenediamine. The sorption rate and capacity of the modified copolymer, p(GME)-en for Rh(III), Au(III) and Pt(IV) ions were determined in batch experiments under non-competitive conditions. The uptake of Rh(III) was faster than those of Au(III) and Pt(IV). The sorption capacity for Pt(IV) was determined in the pH range 0.9–6.0. The maximum Pt(IV) uptake capacity onto p(GME)-en at pH 5.5 was 1.30 mmol/g.

Keywords: macroporous copolymers, modification, sorption, noble metals.

INTRODUCTION

The synthesis of crosslinked macroporous copolymers incorporating chemically immobilised ligands which are highly selective towards noble and platinum group metals is of great interest due to their potential application in the industrial separation and concentration of these valuable metals.[1] Homo- and copolymers with attached ligands containing N, O and S as donor atoms, which are known as effective extractants for the separation of precious metals from base metals, are suitable for the removal of platinum group metals and gold.[2–4] Macroporous hydrophilic copolymers based on glycidyl methacrylate, GMA, produced by radical suspension copolymerization in the shape of regular beads of required size, are versatile starting materials for the synthesis of chelating ion exhangers.[5–11] Namely, these copolymers modified by reaction with

* Author for correspondence. Tel./Fax: +38111-635-839.
# Serbian Chemical Society active member

various amines possess good selectivity and high capacity for platinum group metals, combined with chemical and mechanical stability.[5,6,12–14]

In this paper, the results obtained during the investigation of the sorption rate and capacity of macroporous crosslinked poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) copolymer with attached ethylenediamine, EDA, as a ligand [abbreviated p(GME)-en], for Rh(III), Au(III) and Pt(IV), as well as the pH dependence of Pt(IV) ions sorption under non-competitive conditions, are reported.

EXPERIMENTAL

Analysis and spectroscopy

All reagents and solvents were purchased from commercial sources and used without further purification. Metal salt solutions were prepared from analytical grade reagents, as were the buffer solutions NaCl/HCl (pH 0.9–2.3) and NaOAc/HOAc (pH 2.5–6.0).

The epoxy group content in the synthesized p(GME) sample was determined by the HCl-dioxane method.[15] Elemental analyses (C, H and N) were performed at the Microanalysis Laboratory at the Department of Chemistry, University of Belgrade. The pore size distribution of the synthesized samples was determined by mercury porosimetry using a Carlo Erba Model 2000 instrument. The Pt(IV) concentration was determined by Inductively Coupled Plasma (ICP-OES, Perkin Elmer, Model ICP\6500). Other metals were determined by Atomic Absorption Spectrometry (AAS, SpektrAA Varian Instruments). The IR spectra were recorded in KBr pellets on a Perkin-Elmer FT-IR 1725X spectrophotometer (4000–400 cm^{-1}).

Preparation of p(GME)

The sample of macroporous p(GME) copolymer was prepared by radical suspension copolymerization as described elsewhere.[16] The synthesized sample was purified by Soxhlet extraction using ethanol. The sample prepared in this way was labeled as SGE-10/12. For further investigations, the fraction with particle size of 150–500 μm was used.

Preparation of p(GME)-en

Modification of synthesized copolymer sample with ethylene diamine was carried out in toluene at 70 ºC for 7 h, with a tenfold excess of the diamine. The modified sample was filtered, washed with ethanol, dried and labeled as SGE-10/12-en (the additional label -en designates a sample modified with ethylene diamine).

Metal-sorption experiments

The sorption rate and capacity of p(GME)-en for noble metals from aqueous solutions were investigated in batch experiments under non-competitive conditions. The initial concentration of the metals was either 0.01 or 0.05 M. The capacities for platinum ions were determined as a function of pH by contacting 0.2 g of the modified copolymer with a mixture of 25 ml of the metal salt solution (0.05M) and 25 ml of buffer (NaCl/HCl; pH 0.9–2.3 and NaOAc/HOAc; pH 2.5–6.0). After the predetemined period of time, the samples were filtered, washed sequentially with water and ethanol and then dried. The remaining solutions were kept for metal analysis.

For the sorption rate determination, 1.0 g of copolymer was contacted with 100 ml of an aqueous acid solution of a noble metal ($HAuCl_4$, $PtCl_4$ or Na_3RhCl_6). After appropriate times, 1 ml aliquots were removed and diluted to 100 ml. The concentrations of the metal ions in the aqueous phases after the desired treatment periods were measured by atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

Relevant structural and physical data of the starting p(GME) sample SGE-10/12, are given in Table I.

TABLE I. Porosity parameters (specific pore volume, V_S, specific surface area, S_{Hg}, and pore diameter which corresponds to half of the pore volume, $d_{V/2}$) and epoxy group content on the surface of SGE-10/12.

Sample	V_S / cm^3/g	S_{Hg} / m^2/g	$d_{V/2}$ / nm	Epoxy-group content/mmol/g
SGE-10/12	0.610	50	53	2.08

The porosity parameters (specific pore volume, V_S, specific surface area, S_{Hg}, and pore diameter which corresponds to half of the pore volume, $d_{V/2}$) of the synthesized p(GME) sample were calculated from the cumulative pore volume distribution. The total content of epoxy groups was 4.22 mmol/g, while the epoxy-group content on the surface of the crosslinked copolymer, determined by the HCl–dioxane method, was 2.08 mmol/g. The elemental analysis of p(GME)-en yielded: C, 51.0 %; H, 8.1 % and N, 8.21 %. From these data, the degree of conversion of epoxy groups was calculated to be 69 %, which corresponds to a ligand concentration of 2.93 mmol/g. As shown by Horak *et al.*, IR spectroscopy reveals all the epoxy groups present in the copolymer particles, irrespective of their accessiblity.[17] The epoxy peaks found in the spectrum of p(GME) at 850, 910 cm^{-1} (epoxy ring vibrations), 1250 and 1460 cm^{-1} [δ(CH) epoxy], did not totally disappear from the spectrum of p(GME)-en, indicating incomplete conversion of the epoxy groups. However, the bands found at 3500 cm^{-1} [ν(NH_2)], 1640 cm^{-1} [δ(NH_2), δ(NH)] 1560 cm^{-1} [δ(NH)], 1390 cm^{-1} [ν(NH)] and 1260 and 1460 cm^{-1} [ν(CN)], indicate the presence of –NH and –NH_2 groups as a result of the modification of p(GME) with ethylene diamine.

Besides the removal of metals from waste waters, the recovery of platinum and noble metals is of economical and environmental importance. The advantage of macroporous hydrophilic copolymers based on glycidyl methacrylate modified with various amines over ion exchange resins lies in the fact that, depending on pH, they can both coordinate gold and platinum metals and, acting as basic ion exchangers, bind them as chloro complexes, such as $[AuCl_4]^-$, $[PdCl_4]^{2-}$, $[PtCl_6]^{2-}$, $[RhCl_6]^{3-}$ and $[IrCl_6]^{2-}$.[12] The separation of metal ions on these modified copolymers is determined by the reaction conditions (pH, presence of other ions which compete for the active sites) and structural properties of the chelating copolymers (copolymer particle size, porosity, specific surface area), as well as by the different kinetic and thermodynamic stability of the formed metal complexes with the chemically bonded amine ligands.[13,18] These differences in the stability of ligand–platinum metal complexes are applicable, for instance, for the separation of platinum and rhodium from palladium on macroporous crosslinked poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) copolymer modified with diethylamine.[13] Namely, the platinum and rhodium chloro complexes remain bound on the modified copolymer, while Pd(II) is desorbed by strong acids.

The capacity of chelating copolymers towards metal ions is markedly dependent on pH . Bearing this in mind, the Pt(IV) uptake capacities of the p(GME)-en were determined under non-competitive conditions as a function of pH in buffered solutions. The results are presented in Fig. 1.

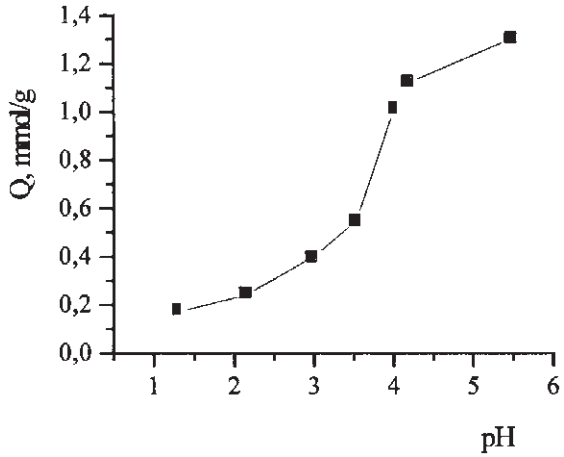

Fig. 1. Capacities of SGE-10/12-en for Pt(IV) ions under non-competitive conditions as a function of pH (sorption time 30 minutes, Pt(IV) initial concentration 0.05 M).

As can be seen, the amount of Pt(IV) ions sorbed per unit mass of the modified copolymer sample (sorption capacity, *Q*, mmol/g) increases with increasing pH and reaches a maximum which represents saturation of the active points (available for metal ions) on the copolymer beads. The maximum uptake capacity of Pt(IV) on the p(GME)-en under non-competitive conditions was 1.30 mmol/g, at pH 5.5.

From the standpoint of potential applications, one of the most important properties is the rapidity of the metal ion uptake. For this reason, the sorption rates for Rh(III), Pt(IV) and Au(III) were determined for SGE-10/2-en and the results are presented in Fig. 2. The reproducibility of the obtained results was verified in duplicate, which indicated the uncertainty of the experimental data to be ± 0.03 mmol/g for Rh(III) sorption and 0.01 mmol/g for Au(III) and Pt(IV) sorption.

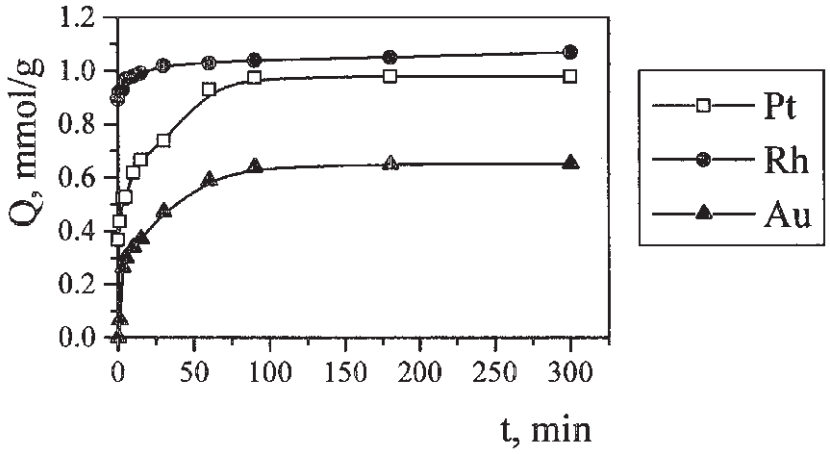

Fig. 2. Sorption of Rh(III), Pt(IV) and Au(III) *vs.* time, on SGE-10/12-en (initial concentration of the metal ions 0.01 M).

The sorption of Rh(III), Pt(IV) and Au(III) on macroporous p(GME)-en was found to be relatively rapid. This can be ascribed to the numerous hydrophilic hydroxyl groups in

the crosslinked macroporous copolymer, which facilitate the interaction of the copolymer with the solution, as well as the coordination of the metal ions due to the presence of heteroatoms (N and O).[1] Also, the results presented in Fig. 2 show that the uptake of Rh(III) was faster than those of Au(III) and Pt(IV). Namely, already after five minutes, approximately 90 % Rh(III), 57 % of Pt(IV) and 46 % of Au(III) had been sorbed, while the equilibrium was established within 30 min. The different rates of sorption of Rh(III), Au(III) and Pt(IV) could be applied for their separation. Also, the desorption of Rh(III) with strong acids (such as HCl and H_2SO_4) is very difficult and incomplete, due to strong coordination with the modified copolymer. Our earlier experiments showed that p(GME)-en under non-competitive conditions can bind five to eight times more platinum than copper and nickel ions and five times more platinum than copper from their mixed chloride solutions.[19] These results indicate that p(GME)-en can be effectively used for the separation of platinum metals from less noble ones and simultaneously from each other.

CONCLUSIONS

In this paper, the sorption ability of macroporous crosslinked poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) modified with ethylene diamine, p(GME)-en, towards platinum metals and gold was investigated. The results show that p(GME)-en can be effectively used for the sorption of Rh(III), Au(III) and Pt(IV) ions. Moreover, due to the different sorption rates, Rh(III), Au(III) and Pt(IV) ions can be selectively sorbed from mixed solutions.

Acknowledgement: This work was supported by the Serbian Ministry of Science, Technology and Development, Grant No 1948.

ИЗВОД

ВЕЗИВАЊЕ ПЛЕМЕНИТИХ МЕТАЛА ЗА МАКРОПОРОЗНИ ПОЛИ(GMA-co-EGDMA) КОПОЛИМЕР МОДИФИКОВАН СА ЕТИЛЕНДИАМИНОМ

А. НАСТАСОВИЋ[1], С. ЈОВАНОВИЋ[2], Д. ЈАКОВЉЕВИЋ[1], С. СТАНКОВИЋ[2] и А. ОЊИА[3]

[1]ИХТМ – Центар за хемију, Његошева 12, Београд, [2]Технолошко-металуршки факултет, Карнегијева 4, Београд и [3]Институт за нуклеарне науке "Винча", Лабораторија за хемијску динамику и зрачење, п. пр. 522, Београд

Умрежени макропорозни поли(глицидилметакрилат-ко-етиленгликолдиметакрилат) синтетизован је суспензионом кополимеризацијом и модификован реакцијом бочних епоксидних група са етилендиамином. Брзина сорпције и капацитет модификованог кополимера, поли(GME)-en, за сорпцију Rh(III), Au(III) и Pt(IV) јона одређени су шаржним експериментима при некомпетитивним условима. Утврђено је да је сорпција Rh(III) јона на поли(GME)-en бржа од сорпције Au(III) и Pt(IV) јона. Капацитет сорпције Pt(IV) јона одређен је у опсегу pH 0,9 – 6,0. Максимална количина Pt(IV) јона везаних за p(GME)-en при pH 5,5 износи 1,30 mmol/g.

(Примљено 28. јула 2003, ревидирано 8. јануара 2004)

REFERENCES

1. J. M. Sanchez, M. Hidalgo, V. Salvado, *React. Funct. Polym.* **49** (2001) 215
2. J. M. Sanchez, M. Hidalgo, M. Valiente, V. Salvado, *J. Polym. Sci.: Polym. Chem.* **38** (2000) 269
3. E. Antico, A. Masana, V. Salvado, J. Havel, M. Valiente, *Anal. Chim. Acta* **296** (1994) 325
4. R. A. Beauvais, S. D. Alexandratos, *React. Funct. Polym.* **36** (1998) 113
5. *Synthesis and Separations Using Functional Polymers*, D. C. Sherrington and P. Hodge, Eds., Wiley, London, 1988
6. D. Lindsay, D. C. Sherrington, J. Greig, R. Hancock, *J. Chem. Soc., Chem. Commun.* (1987) 1270
7. F. Švec, E. Kalalova, J. Kalal, *Angew. Makromol. Chem.* **136** (1985) 183
8. P. M. van Berkel, W. L. Driessen, F. J. Parlevliet, J. Reedijk, D. C. Sherrington, *Eur. Polym. J.* **33** (1997) 129
9. P. M. van Berkel, S. C. van der Slot, W. L. Driessen, J. Reedijk, D. C. Sherrington, *Eur. Polym. J.* **33** (1997) 303
10. P. M. van Berkel, M. Punt, G. J. A. A. Koolhaas, W. L. Driessen, J. Reedijk, D. C. Sherrington, *React. Funct. Polym.* **32** (1997) 139
11. B. Senkal, N. Bicak, *React. Funct. Polym.* **49** (2001) 151
12. E. Kalalova, P. Thuy, *Angew. Makromol. Chem.* **180** (1990) 159
13. J. Kalal, E. Kalalova, J. Landova, F. Švec, *Angew. Makromol. Chem.* **115** (1983) 13
14. Z. Radova, E. Kalalova, J. Kalal, Yu. N. Kukuskin, S. A. Simanova, L. V. Konovalov, V. N. Pak, *Angew. Makromol. Chem.* **81** (1979) 55
15. G. M. Kline, *Analytical Chemistry of Polymer*, Interscience, New York 1959, p. 127
16. S. Jovanović, A. Nastasović, N. Jovanović, K. Jeremić, Z. Savić, *Angew. Makromol. Chem.* **219** (1994) 161
17. D. Horak, J. Labsky, J. Pilar, M. Bleha, Z. Pelcbauer, F. Švec, *Polymer* **34** (1993) 3481
18. A. Denizli, B. Salih, E. Piskin, *React. Funct. Polym.* **29** (1996) 11
19. S. Jovanović, A. Nastasović, N. N. Jovanović, T. Novaković, Z. Vuković, K. Jeremić, *Hem. Ind.* **54** (2000) 471.